

APPLICATION FOR UNITED STATES PATENT

in the name of

**Todd Bofinger, William Bowden, Rimma Sirotina, and Fan
Zhang**

for

Cathode Material for Lithium Battery

Fish & Richardson P.C.
1425 K Street, N.W.
11th Floor
Washington, DC 20005-3500
Tel.: (202) 783-5070
Fax: (202) 783-2331

ATTORNEY DOCKET:

08935-301001 / M-5064

Cathode Material for Lithium Battery

TECHNICAL FIELD

This invention relates to a cathode material for lithium batteries.

BACKGROUND

Batteries are commonly used electrical energy sources. A battery contains a negative
5 electrode, typically called the anode, and a positive electrode, typically called the cathode.
The anode contains an active material that can be oxidized; the cathode contains or consumes
an active material that can be reduced. The anode active material is capable of reducing the
cathode active material.

When a battery is used as an electrical energy source in a device, electrical contact is
10 made to the anode and the cathode, allowing electrons to flow through the device and
permitting the respective oxidation and reduction reactions to occur to provide electrical
power. An electrolyte in contact with the anode and the cathode contains ions that flow
through the separator between the electrodes to maintain charge balance throughout the
battery during discharge.

SUMMARY

15 In general, a lithium battery includes a cathode including lithiated manganese
dioxide.

In one aspect, a method of making a lithiated manganese dioxide for a primary
lithium battery includes contacting a manganese dioxide with a lithium ion source at a
20 lithiation temperature sufficient to substantially replace protons in the manganese dioxide
with lithium ions, and heating the manganese dioxide at a water removal temperature
sufficient to substantially remove residual and surface water to produce a lithiated manganese
dioxide having an X-ray diffraction pattern substantially similar to the X-ray diffraction
pattern of the manganese dioxide prior to lithiation.

25 In another aspect, a method of making a cathode for a battery includes contacting a
manganese dioxide with a lithium ion source, heating the manganese dioxide to produce a
lithiated manganese dioxide having an X-ray diffraction pattern substantially similar to the
X-ray diffraction pattern of the manganese dioxide prior to lithiation, and coating a current

collector with a composition including a carbon source, and the cathode active material, wherein the cathode active material includes the manganese dioxide.

In another aspect, a primary lithium battery includes an anode including a lithium-containing anode active material, a cathode including a lithiated manganese dioxide having
 5 an X-ray diffraction pattern substantially similar to the X-ray diffraction pattern of the manganese dioxide prior to lithiation, and a separator between the anode and the cathode.

The manganese dioxide can be persulfate derived chemical manganese dioxide, an electrochemical manganese dioxide, or gamma-manganese dioxide. The lithium ion source can be an aqueous solution including a lithium salt, such as a lithium hydroxide. The
 10 lithiation temperature can be between 40 C and 100 C. The water removal temperature can be between 180 C and 500 C, for example, between 200 C and 460 C.

In the battery, the lithium-containing anode active material can be lithium or a lithium alloy. The battery can include a nonaqueous electrolyte in contact with the anode, the cathode and the separator. The nonaqueous electrolyte can include an organic solvent. The
 15 lithiated gamma-manganese dioxide can have an X-ray diffraction pattern having peaks near 24 and 32 degrees 2-theta (CuK α radiation) and can have substantially all or most of the proton content normally present in gamma-manganese dioxide replaced by lithium ions. The battery can have high current capability and discharge capacity greater than a lithium/manganese dioxide battery including heat-treated manganese dioxide (HEMD).

The lithiated manganese dioxide can be used in a Li/MnO₂ battery that possesses improved capacity and running voltage in high drain conditions and can have reduced gas evolution compared to conventional Li/MnO₂ batteries. For example, the lithiated gamma-manganese dioxide can be suitable for use in batteries for digital cameras. A primary lithium battery including the lithiated manganese dioxide can have high running voltage, current
 25 capability and discharge capacity compared to a lithium/manganese dioxide battery including heat treated manganese dioxide (HEMD). The lithiated manganese dioxide can also evolve less gas during storage in a battery. The lithiated manganese dioxide has a low surface area and high electrical performance. The lithiated manganese dioxide has an X-ray diffraction pattern substantially identical to that of the parent manganese dioxide starting material even
 30 though the proton content of the manganese dioxide has been substantially completely replaced with lithium.

The details of one or more embodiments are set forth in the accompanying drawings and the description below. Other features, objects, and advantages will be apparent from the description and drawings, and from the claims.

DESCRIPTION OF DRAWINGS

5 FIG. 1 is a schematic drawing of a battery.

FIG. 2A is a representative X-ray diffraction pattern of highly proton containing gamma-manganese dioxide.

FIG. 2B is a representative X-ray diffraction pattern of a lithium exchanged gamma-manganese dioxide dried between 200 and 400 C of the present invention.

10 FIG. 2C is a representative X-ray diffraction pattern of a heat-treated manganese dioxide (HEMD)

FIG. 2D is a representative X-ray diffraction pattern of a persulphate prepared manganese dioxide (p-CMD).

15 FIG. 2E is a representative X-ray diffraction pattern of a heat-treated lithiated persulphate prepared manganese dioxide (Li-p-CMD).

FIG. 2F is a representative X-ray diffraction pattern of a heat treated lithium exchanged manganese dioxide of U.S. Patent 6,190,800.

20 FIGS. 3A is the capacity spectrum of heat treated manganese dioxide (HEMD) and lithium treated persulphate prepared manganese dioxide (Li-p-CMD) as a function of discharge voltage.

FIG. 3B is a representative electrochemical spectrum of lithiated persulphate manganese dioxide and heat-treated manganese dioxide.

FIG. 3C is a representative electrochemical spectrum of lithiated persulfate manganese dioxide and persulfate manganese dioxide.

25 FIG. 3D is a representative electrochemical spectrum of lithiated gamma-manganese dioxide and lithium containing heat treated manganese dioxide.

DETAILED DESCRIPTION

Referring to FIG. 1, a primary lithium electrochemical cell 10 includes an anode 12 in electrical contact with a negative lead 14, a cathode 16 in electrical contact with a crown 18, 30 a separator 20 and an electrolyte. Anode 12, cathode 16, separator 20 and the electrolyte are

contained within housing 22. The electrolyte can be a solution that includes a solvent system and a salt that is at least partially dissolved in the solvent system. One end of housing 22 is closed with a positive external contact 24 and an annular insulating gasket 26 that can provide a gas-tight and fluid-tight seal. Crown 18 and positive lead 28 can connect cathode
 5 16 to positive external contact 24. A safety valve is disposed in the inner side of positive external contact 24 and is configured to decrease the pressure within battery 10 when the pressure exceeds some predetermined value. In certain circumstances, the positive lead can be circular or annular and be arranged coaxially with the cylinder, and include radial extensions in the direction of the cathode. Electrochemical cell 10 can be, for example, a
 10 cylindrical wound cell, a button or coin cell, a prismatic cell, a rigid laminar cell or a flexible pouch, envelope or bag cell.

Anode 12 can include alkali and alkaline earth metals, such as lithium, sodium, potassium, calcium, magnesium, or alloys thereof. The anode can include alloys of alkali or alkaline earth metals with another metal or other metals, for example, aluminum. An anode
 15 including lithium can include elemental lithium, a lithium-insertion compound, or lithium alloys, or combinations thereof.

The electrolyte can be a nonaqueous electrolyte solution including a solvent and a salt. The electrolyte can be a liquid or a polymeric electrolyte. The salt can be an alkali or alkaline earth salt such as a lithium salt, a sodium salt, a potassium salt, a calcium salt, a
 20 magnesium salt, or combinations thereof. Examples of lithium salts include lithium hexafluorophosphate, lithium tetrafluoroborate, lithium hexafluoroarsenate, lithium perchlorate, lithium iodide, lithium bromide, lithium tetrachloroaluminate, lithium trifluoromethanesulfonate, $\text{LiN}(\text{CF}_3\text{SO}_2)_2$, and $\text{LiB}(\text{C}_6\text{H}_4\text{O}_2)_2$. A perchlorate salt such as lithium perchlorate can be included in the electrolyte to help suppress corrosion of aluminum
 25 or an aluminum alloy in the cell, for example in the current collector. The concentration of the salt in the electrolyte solution can range from 0.01 molar to 3 molar, from 0.5 molar to 1.5 molar, and in certain embodiments can be 1 molar.

The solvent can be an organic solvent. Examples of organic solvents include carbonates, ethers, esters, nitriles and phosphates. Examples of carbonates include ethylene
 30 carbonate, propylene carbonate, diethyl carbonate and ethylmethyl carbonate. Examples of ethers include diethyl ether, dimethyl ether, dimethoxyethane, diethoxyethane and tetrahydrofuran. Examples of esters include methyl propionate, ethyl propionate, methyl

butyrate and gamma-butyrolactone. Examples of nitriles include acetonitrile. Examples of phosphates include triethylphosphate and trimethylphosphate. The electrolyte can be a polymeric electrolyte.

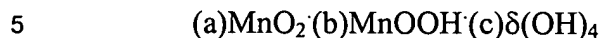
Separator 20 can be formed of any separator material used in lithium primary or secondary battery separators. For example, separator 20 can be formed of polypropylene, polyethylene, polytetrafluoroethylene, a polyamide (e.g., a nylon), a polysulfone, a polyvinyl chloride, or combinations thereof. Separator 20 can have a thickness of from about 12 microns to about 75 microns and more preferably from 12 to about 37 microns. Separator 20 can be cut into pieces of a similar size as anode 12 and cathode 16 and placed therebetween as shown in FIG. 1. The anode, separator, and cathode can be rolled together, especially for use in cylindrical cells. Anode 12, cathode 16 and separator 20 can then be placed within housing 22 which can be made of a metal such as nickel or nickel plated steel, stainless steel, aluminum-clad stainless steel, aluminum, or an aluminum alloy or a plastic such as polyvinyl chloride, polypropylene, a polysulfone, ABS or a polyamide. Housing 22 containing anode 12, cathode 16 and separator 20 can be filled with the electrolytic solution and subsequently hermetically sealed with positive external contact 24 and annular insulating gasket 26.

Cathode 16 includes a composition that includes a lithiated manganese dioxide. The lithiated manganese dioxide can be prepared by treating a persulfate derived chemical manganese dioxide or gamma-manganese dioxide with a lithium ion source to replace the protons of the manganese dioxide with lithium ions. Preparation of persulfate derived chemical manganese dioxide (p-CMD) is described, for example, in U.S. Patent Nos. 5,277,890, 5,348,728 and 5,482,796, each of which is incorporated by reference in its entirety. Preparation of heat treated manganese dioxide is described, for example, in U.S. Patent No. 4,133,856, which is incorporated by reference in its entirety. Gamma-manganese dioxide is described, for example, in "Structural Relationships Between the Manganese (IV) Oxides", Manganese Dioxide Symposium, 1, The Electrochemical Society, Cleveland, 1975, pp. 306-327, which is incorporated herein by reference in its entirety. The lithium ion source can be an aqueous solution including a lithium salt, such as, for example, lithium hydroxide. The lithium ion exchange can be performed at a temperature above room temperature, for example, between 40 C and 120 C, or at or between 60 C and 100 C.

The lithium-exchanged material is then heated to remove residual and surface moisture. The material can be heated in air, in oxygen, in inert atmosphere, or in a vacuum.

The material can be heated to a temperature greater than 150 C, greater than 180 C, less than 500 C, or less than 480 C. This can convert the manganese dioxide to a lithiated gamma manganese dioxide phase or to a ramsdellite LiMD phase.

Gamma manganese dioxide can have the formula:



where the delta is used to indicate a cation vacancy in the Mn (IV) lattice. For example, in one composition, (a) is 0.9, (b) is 0.06, and (c) is 0.04. About half of the lattice protons in the manganese dioxide are replaced with lithium ions by exposing the manganese dioxide to aqueous lithium hydroxide at pH 13 at ambient temperature as disclosed in U. S. patent 6,190,800, which is incorporated by reference in its entirety. By performing the lithium exchange at higher temperature, for example, at 60 C or 100 C, it is possible to reduce or avoid destruction of cation vacancy sites and increase lithium uptake to replace 75 % or more of the protons originally present in the gamma-manganese dioxide.

In certain circumstances, the p-CMD can have a low BET surface area, for example, below 30 m²/gram. Other manganese dioxide materials that can be treated by this process can include alternative forms of gamma-manganese dioxide of artificial ramsdellite character, such as, for example, gamma-manganese dioxide materials derived by acid leaching of LiMn₂O₄ spinels, and by acid treatment of Mn₂O₃ and Mn₃O₄ may be suitable, or lambda-manganese dioxides. A stabilization of the lithiated manganese dioxide phase produced by heating lithiated p-CMD can be attributed, in part, to the high lithium content brought about by a high cation vacancy concentration. Accordingly, other manganese dioxide materials having a high cation vacancy level can be used in this process. In addition, under certain conditions, elevating the lithiation temperature can advantageously increase the lithium ion content of the material. For example, a lithium level of about Li_{0.22}MnO₂ heat treated for 6 hours at 200 C in air can form a material with BET surface area of about 15 m²/g. The material of choice can distinguished as having an X-ray diffraction pattern characteristic of gamma-manganese dioxide rather than the HEMD commonly used for Li cells.

The cathode composition can also include a binder, for example, a polymeric binder such as PTFE, PVDF, Kraton or Viton (e.g., a copolymer of vinylidene difluoride and hexafluoropropylene). The cathode composition can also include a carbon source, such as,

for example, carbon black, synthetic graphite including expanded graphite or non-synthetic graphite including natural graphite, an acetylenic mesophase carbon, coke, graphitized carbon nanofibers or a polyacetylenic semiconductor.

The cathode includes a current collector on which the cathode active material can be coated or otherwise deposited. The current collector can have a region in contact with positive lead 28 and a second region in contact with the active material. The current collector serves to conduct electricity between the positive lead 28 and the active material. The current collector can be made of a material that is strong and is a good electrical conductor (i.e. has a low resistivity), for example a metal such as stainless steel, titanium, aluminum or an aluminum alloy. One form that the current collector can take is an expanded metal screen or grid, such as a non-woven expanded metal foil. Grids of stainless steel, aluminum or aluminum alloy are available from Exmet Corporation (Branford, CT).

In general, a cathode is made by coating a cathode material onto a current collector, drying and then calendering the coated current collector. The cathode material is prepared by mixing an active material together with other components such as a binder, solvent/water, and a carbon source. The current collector can include a metal such as titanium, stainless steel, aluminum, or an aluminum alloy. The current collector can be an expanded metal grid. To form the cathode material, an active material such as manganese dioxide can be combined with carbon, such as graphite and/or acetylene black, and mixed with small amount of water. The current collector is then coated with the cathode slurry.

In a cylindrical cell, the anode and cathode are spirally wound together with a portion of the cathode current collector extending axially from one end of the roll. The portion of the current collector that extends from the roll can be free of cathode active material. To connect the current collector with an external contact, the exposed end of the current collector can be welded to a metal tab, which is in electric contact with an external battery contact. The grid can be rolled in the machine direction, the pulled direction, perpendicular to the machine direction, or perpendicular to the pulled direction. The tab can be welded to the grid to minimize the conductivity of grid and tab assembly. Alternatively, the exposed end of the current collector can be in mechanical contact (i.e. not welded) with a positive lead which is in electric contact with an external battery contact. A cell having a mechanical contact can require fewer parts and steps to manufacture than a cell with a welded contact. The mechanical contact can be more effective when the exposed grid is bent towards the center of

the roll to create a dome or crown, with the highest point of the crown over the axis of the roll, corresponding to the center of a cylindrical cell. In the crown configuration, the grid can have a denser arrangement of strands than in the non-shaped form. A crown can be orderly folded and the dimensions of a crown can be precisely controlled.

5 The positive lead 28 can include stainless steel, aluminum, or an aluminum alloy. The positive lead can be annular in shape, and can be arranged coaxially with the cylinder. The positive lead can also include radial extensions in the direction of the cathode that can engage the current collector. An extension can be round (e.g. circular or oval), rectangular, triangular or another shape. The positive lead can include extensions having different shapes.

10 The positive lead and the current collector are in electrical contact. Electrical contact between the positive lead and the current collector can be achieved by mechanical contact. Alternatively, the positive lead and current collector can be welded together. The positive lead and the cathode current collector are in electrical contact. The electrical contact can be the result of mechanical contact between the positive lead and current collector.

15 Example 1 (Lithiated p-CMD)

p-CMD was prepared as follows. Manganous sulfate (239 grams, 1.6 moles) was dissolved in 1.8 L water and sodium persulfate (346 grams 1.45 moles) as added and stirred to dissolve. The solution was heated with stirring to 55 C. After 5 hours the pH is 0.98 and considerable black solids were present in solution. The heat was removed and the solution

20 allowed to stand overnight. LiOH solid was added to neutralize the acid created in the oxidation process, reaching a pH of 1.14. The solution was then heated to 84 C and pH drops to 0.48 through the day. A second neutralization with LiOH is carried out to a pH of 2.05. The solution was then heated to 90 C for one hour, allowed to cool and collected on a fritted glass filter. The collected precipitate was dried at 60 C overnight to form a cake that was

25 dispersed in water and filtered to form a finely divided powder. Total yield of product was about 129 grams; 1.48 moles.

Lithium exchange was performed on the p-CMD as follows. p-CMD (50 grams, 0.6 moles) was dispersed in 50 ml deionized water and solid LiOH.H₂O (3.4 g, 0.08 moles) was added with continual stirring. The final pH reached after about 1 hours was 12.6. The slurry

30 of MnO₂ in LiOH solution was put aside to stay overnight at high pH. The slurry was then filtered through a pressure filter to isolate the lithium-exchanged p-CMD. The wet p-CMD was left overnight to dry at room temperature, and was then dried at 60 C. Total yield of

product is about 50.7 grams, 0.6 moles. The X-ray diffraction pattern of the persulphate prepared manganese dioxide is shown in FIG. 2D. The lithium-exchanged p-CMD was then heat treated at 350 C for 1 hour to produce the lithiated persulphate-manganese dioxide. The X-ray diffraction pattern of the lithiated persulphate-manganese dioxide was nearly identical to the pattern shown in FIG. 2E. In other examples, the lithiated p-CMD was heat treated at 450 C for different lengths of time.

Example 2 (Lithiated gamma-manganese dioxide)

EMD (Kerr-McGee High Power alkaline grade MnO_2)(300 g) was placed in a 2 L beaker and dispersed with about 1 L water. Sulfuric acid was added to remove exchangeable sodium. The suspension of MnO_2 in acid was filtered and the filtrate discarded leaving and acid-washed, sodium free MnO_2 as described in U.S. patent 5,698,176. The manganese dioxide was again dispersed in water, heated to 60 C on a hot plate and solid $\text{LiOH} \cdot \text{H}_2\text{O}$ (30.7 grams) was added with continual stirring while the pH was monitored. In contrast to lithiation at room temperature, where the nominal pH 13 was attained, the suspension remained at a pH of about 11.3. The slurry of MnO_2 in LiOH solution was put aside and allowed to stand overnight. The pH was then adjusted to the target pH of 12.5 with more solid lithium hydroxide. The slurry was then filtered through a fine porosity glass fritted filter or a pressure filter to isolate the lithium-exchanged manganese dioxide. The wet manganese dioxide was then dried overnight at 100 C to provide a dark brown powder. The observed lithium uptake corresponds to 0.21 Li per mole of MnO_2 . To remove residual surface and lattice moisture the MnO_2 was then dried at 200 C for 6 hours. The 200 C drying temperature was selected since solid state MAS ^6Li NMR measurements had shown that both Li and protons in EMD were mobile at 200 C. As shown by comparison of FIG. 2A (protonated gamma-manganese dioxide from Kerr-McGee) and Figure 2B, the lithiated gamma-manganese dioxide was in the γ -phase after drying at 200 C.

Comparative Example 1(HEMD)

Delta EMD lithium grade MnO_2)(1200 g) was placed in an oven and heated under flowing air at 350 degrees C for a period of 7 hours. The temperature of the oven was gradually increased to reach 350 degrees over a 6 hours period followed by 7 hours at 350 C. The resulting material, HEMD has an X-ray diffraction pattern shown in Figure 2C and is

considered as being substantially the material of U.S. patent 4,133,856. This material is used as comparative Example 1 in subsequent Examples.

Comparative Example 2 (Lithiated heat treated manganese dioxide (LiMD))

Kerr-McGee High Power alkaline grade EMD or Delta EMD lithium grade
5 MnO_2 (1200 g) was placed in a 2 L beaker and dispersed with about 1 L water. Solid $\text{LiOH} \cdot \text{H}_2\text{O}$ was added with continual stirring while the pH was monitored. When the desired pH near 12.5 was reached the slurry of MnO_2 in LiOH solution was put aside and allowed to stand overnight. The pH was then adjusted to the target pH of 12.5 with more solid lithium hydroxide. The overnight stand in lithium hydroxide solution can allow the diffusion of
10 protons and lithium ions within the manganese dioxide to equilibrate and allow maximum replacement of protons by lithium. The slurry was then filtered through a fine porosity glass fritted filter or a pressure filter to isolate the lithium-exchanged manganese dioxide. The wet manganese dioxide was then dried overnight at 100 C to provide a dark brown powder. To remove residual surface and lattice moisture the MnO_2 was then dried at 350 C for 6 hours in
15 air. The temperature can be raised as high as 400 C without changing the product of the reaction, but that heating that causes Mn_2O_3 to be produced, for example, heating to 450 C in air, can indicate a deleterious loss of oxygen has taken place. Again, the lithiated manganese dioxide had a diffraction pattern as represented in FIG. 2F and indicating that it is a material as described in U. S. Patent 6,190,800.

Example 4 (SPECS)

The lithiated gamma-manganese dioxide products of Examples 1-2 were distinguished from heat treated manganese dioxide (HEMD) and lithium exchanged heat treat EMD (LiMD) of Comparative examples 1 and 2 by use of the SPECS low rate discharge test. In the SPECS test a cell is discharged at a constant voltage for a pre-selected period of time, then stepped to a
25 new voltage. SPECS has been described in, for example, A.H. Thompson, Electrochemical Potential Spectroscopy: A New Electrochemical Measurement, J. Electrochemical Society 126(4), 608-616 (1979); Y. Chabre and J. Pannetier, Structural and Electrochemical Properties of the Proton/ γ - MnO_2 System, Prog. Solid St. Chem. 23, 1-130 (1995); and references therein, each of which is hereby incorporated by reference in its entirety. One of
30 the outputs of this experiment is a voltage spectrum that addresses the questions of how quickly a material can discharge at a given voltage.

The SPECS curves of the lithiated gamma-manganese dioxide of Example 2 and HEMD is shown in FIG. 3A. As shown in FIG. 3A, the lithiated gamma-manganese dioxide of Example 1 has a higher initial discharge process centered about 3.25 V and a second discharge process centered about 2.87 V as compared to the single process centered about 2.68 V for the HEMD of comparative Example 1. The high voltage of the material of Example 1 is improved over comparative Example 1 provides a higher running voltage during discharge.

The SPECS curves of the lithiated persulphate-manganese dioxide of Example 1 and HEMD is shown in FIG. 3B. As shown in FIG. 3B, the lithiated persulphate manganese dioxide undergoes a variety of discharge processes with the two most prominent processes centered about 3.07 and 2.94 V vs. the single process centered about 2.68 V seen for HEMD.

The electrochemical spectra of the heat-treated lithiated persulphate manganese dioxide is compared with the SPECS curve of the parent persulphate manganese dioxide in FIG. 3C. As shown in FIG. 3C, the lithiated persulphate manganese dioxide has a higher running voltage after 350 C treatment than the persulphate manganese dioxide after heat treatment.

The electrochemical spectra of heat-treated lithium containing manganese dioxide of Comparative Example 2 and Example 2 of the current invention are presented in FIG. 3D. As shown in FIG. 3D, the Example 1 material shows higher voltage and therefore better running voltage in a battery.

Example 5 (Foil Bag Gas Test)

Gas evolution by the lithiated gamma-manganese dioxide in contact with electrolyte was tested. The foil bag gas tests were conducted on HEMD, the lithiated p-CMD after heat treatment at 350 C of Example 1, lithiated gamma-manganese dioxide after heat treatment to 200 C of Example 2 lithiated -manganese dioxide after heat treatment to 350 C in air for 7 hours of Comparative Example 2 and the HEMD of Comparative Example 1.. In a foil bag gas test, both electrolyte (10 w/o EC 20 w/o PC and 70 w/o DME with 0.6 M LiTFS) (1.8 grams) and the lithiated manganese dioxide (6.5 grams) were sealed in an aluminized Mylar bag and stored at 60 C. Gas evolution was determined by displacement and weight under water. BET surface area was also determined. Results are listed in Table 1 and show the Example 2 lithiated gamma-manganese dioxide produces less gas than either comparative Example 1 or comparative Example 2 and that the Example 1 lithiated persulphate manganese dioxide of Example 1 produces only slightly more gas than comparative Examples 1 and 2.

TABLE 1

Property	HEMD (Comparative Example 1)	Lithiated p-CMD of Example 1	Lithiated gamma- manganese dioxide of Example 2	Lithiated gamma- manganese dioxide heated to 350 C in air for 7 h (Comparative Example 2)
Li (%)	0.0	0.68	1.19	0.86
Total Mn (%)	61.6	60.9	59.4	60.8
x in MnO _x	1.97	1.95	1.98	1.94
Density (g/cm ³)	4.77	4.57	4.378	4.50
BET surface area (m ² /g)	30.8	37.18	15.7	30.2
Average pore diameter (Å)	92.7	208.4	98.19	76.2
Total pore volume (cm ³ /g)	0.0715	0.1937	0.0366	0.0575
Gas after 1 day (cm ³)	21.5	27.07	7.7	16.01
Gas after 1 week (cm ³)	34.15	44.44	18.24	33.15
Gas after 2 weeks (cm ³)	40.61	54.6	24.68	39.94
Gas after 4 weeks relative to HEMD (%)	-	138	70	108

Example 6 (Scaled Optio Tests)

Electrochemical performance of 2430-size coin cells including the lithiated gamma-manganese dioxide cathode material and a lithium anode was tested. The Optio test conditions are summarized in Table 2.

Table 2

Function	FLASH ON - LCD ON					FLASH OFF - LCD ON				
	Step #	Actual		2430 (Watts)	Time (s.)	Step #	7-mm, 2/3A (W)		2430 (Watts)	Time (s.)
LCD	Step 1	2.9		0.0829	0.5	Step 1	2.9		0.0829	0.5
Zoom	Step 2	4.87		0.1391	0.5	Step 2	4.87		0.1391	0.5
Process	Step 3	2.9		0.0829	1	Step 3	2.9		0.0829	2
AF	Step 4	4.87		0.1391	0.5	Step 4	4.87		0.1391	0.5
Process	Step 5	2.9		0.0829	1	Step 5	2.9		0.0829	1
Shutter	Step 6	6		0.1714	0.1	Step 6	6		0.1714	0.1
Process	Step 7	2.9		0.0829	1	Step 7	3		0.0857	2.4
Flash Rchg	Step 8	5		0.1429	1					
Process	Step 9	3		0.0857	0.4					
LCD Sby	Step 10	2.9		0.0829	14	Step 8	2.9		0.0829	13
Rest	Step 11	0		0	40	Step 9	0		0	40
Weighted Avg		3.1					3			

One test that was performed was the Optio digital camera test. The Optio test was determined by taking the load regime for the Optio 330 camera and scaling it to fit the 2430

size coin cell. It consists of a series of pulses to simulate the loads place on a battery in service in a camera. Cells were prepared containing HEMD (Comparative Example 1), p-CMD (control), Li-p-CMD of Example 1, and the lithiated manganese dioxide of Example 2 and were tested in fresh conditions. Five to eight cells were tested and the results were averaged. The number of cycles achieved above the threshold voltages of 2.5, 2.0, 1.8 and 1.5 are summarized in Table 3.

Table 3

Manganese dioxide	2.5 V	2.0 V	1.8 V	1.5 V
HEMD	2	174	194	
Standard Deviation	0	44	41	
Confidence		31	28	
p-CMD		277	301	318
Standard Deviation		29	27	21
Confidence		22	20	15
Li-p-CMD (Example 1)	226	331	341	349
Standard Deviation	14	13	13	9
Confidence	11	9	9	6
Lithiated gamma-manganese dioxide (Example 2)	219	287	299	
Standard Deviation	15	17	20	
Confidence	10	12	14	

As shown in Table 2, the Li-p-CMD of Example 1 and the lithiated gamma-manganese dioxide of Example 2 outperformed the HEMD material to the standard cutoff of 2.0 V and delivered more service on higher cutoff voltages. The high performance of the Li-p-CMD of Example 1 and lithiated gamma-manganese dioxide was also demonstrated by the high average running voltage. The lithiated gamma-manganese dioxide offers excellent service even to the 2.5 V cutoff. Initial and final voltage on a high drain step of the Optio protocol was plotted and the voltage at the mid-point of the discharge was taken as a measure of quality of service on the Optio test. When evaluated by this technique, the cells with HEMD has an average load voltage of 2.35 while the cells with Li-p-CMD of Example 1 had an average

voltage of 2.68 (a 330 mV advantage) and the cells with lithiated gamma-manganese dioxide had an average voltage of 2.78 (a 430 mV advantage).

A number of embodiments have been described. Nevertheless, it will be understood that various modifications may be made. Accordingly, other embodiments are within the scope of the following claims.

5